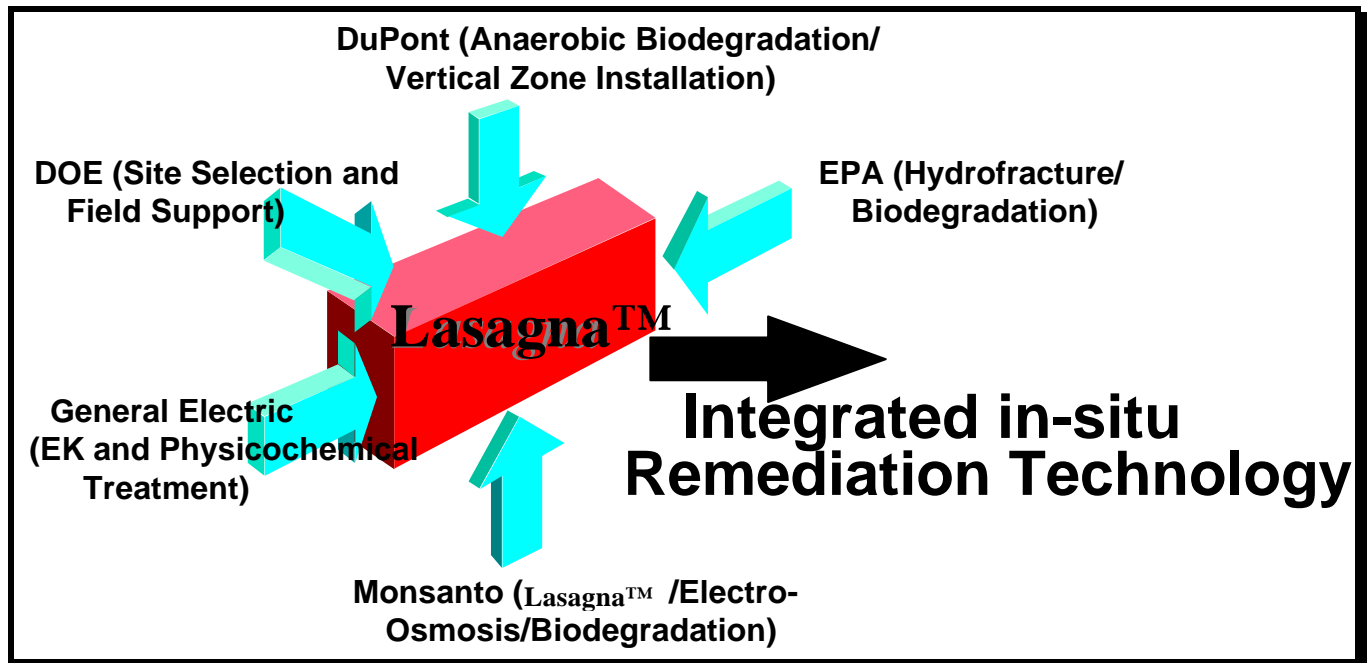# Monsanto

June 1996

Development of an Integrated *in-situ* Remediation Technology

Topical Report for *Task #9 - Part II entitled "TCE Degradation Using Non-Biological Methods"* (September 26, 1994 - May 25, 1996)

Robert G. Orth and David E. McKenzie (Monsanto Company)

DOE Contract Number: DE-AR21-94MC31185

DuPont (Anaerobic Biodegradation/ Vertical Zone Installation)

DOE (Site Selection and Field Support)

EPA (Hydrofracture/ Biodegradation)

Lasagna™

General Electric (EK and Physicochemical Treatment)

Integrated in-situ Remediation Technology

Monsanto (Lasagna™ /Electro- Osmosis/Biodegradation)

Monsanto

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167
Phone: (314) 694-1466
FAX: (314) 694-1531

20 March, 1997

Re: Ordering Information for *"Development of an Integrated in-situ Remediation Technology"* Topical Reports generated under DOE contract number DE-AR21-94MC31185 which was signed September 26, 1994.

Dear Sir/Ms.:

The following table summarizes ordering information for all technical reports written for the above referenced contract. Copies of these reports may be obtained from the Office of Scientific and Technical Information [(423)576-8401] if you are with DOE or a DOE contractor, or from:

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Title	Document Number
• **Topical Report for Task #1 entitled "Evaluation of Treatment Zone Formation Options" (September 26, 1994 - May 25, 1996)** Stephen H. Shoemaker, Richard C. Landis, Ronald J. Griffith, Dale S. Schultz, and Gary E. Quinton (DuPont Company)	**DOE/METC/31185 —5436, DE97002165**
• **Topical Report for Tasks #2-4 entitled "Electrokinetic Modeling" (September 26, 1994 - May 25, 1996)** Andrew P. Shapiro (General Electric Company)	**DOE/METC/31185 —5391, DE97002135**
• **Topical Report for Task #5 entitled "Cost Analysis" (September 26, 1994 - May 25, 1996)** Gary Quinton, Dale Schultz, Richard Landis, Ronald Griffith, and Stephen Shoemaker (DuPont Company)	**DOE/METC/31185 —5389, DE97002134**
• **Topical Report for Task #6 entitled "Lab-Scale Development of Microbial Degradation Process" (September 26, 1994 - May 25, 1996)** J. Martin Odom (DuPont Company)	**DOE/METC/31185 —5388, DE97002130**
• **Topical Report for Task #7 entitled "Development of Degradation Processes" (September 26, 1994 - May 25, 1996)** M. J. Brackin, M. H. Heitkamp and S. V. Ho (Monsanto Company)	**DOE/METC/31185 —5495, DE97002165**
• **Topical Report for Tasks #8 and 10 entitled "Laboratory and Pilot Scale Experiments of the *Lasagna*™ Process" (September 26, 1994 - May 25, 1996)** Sa V. Ho, Christopher J. Athmer, and P. Wayne Sheridan (Monsanto Company) and Andrew P. Shapiro (General Electric Company)	**DOE/METC/31185 —5375, DE97002150**
• **Topical Report for Task #9-Part I entitled "TCE Degradation Using Non-Biological Methods" (September 26, 1994 - May 25, 1996)** Andrew P. Shapiro, Timothy M. Sivavec, and Sunita S. Baghel (General Electric Company)	**DOE/METC/31185 —5392, DE97002133**
• **Topical Report for Task #9 - Part II entitled "TCE Degradation Using Non-Biological Methods" (September 26, 1994 - May 25, 1996)** Robert G. Orth and David E. McKenzie (Monsanto Company)	**DOE/METC/31185 —5393, DE97002131**

• **Topical Report for Task #11 entitled "Evaluation of TCE Contamination Before and After the Field Experiment" (September 26, 1994 - May 25, 1996)** B. Mason Hughes, Sa V. Ho, Christopher J. Athmer, and P. Wayne Sheridan (Monsanto Company) Stephen H. Shoemaker and John R. Larson (DuPont) Jay L. Clausen (LMES) and John L. Zutman (ORNL-Grand Junction)	**DOE/METC/31185 —5496, DE97002166**
• **Topical Report for Tasks #12 and 13 entitled "Large Scale Field Test of the *Lasagna*™ Process" (September 26, 1994 - May 25, 1996)** Christopher J. Athmer, Sa V. Ho, B. Mason Hughes, P. Wayne Sheridan, and P. H. Brodsky (Monsanto Company) Andrew P. Shapiro, Roy F. Thornton, and Joseph J. Salvo (General Electric Company) and Dale S. Schultz, Richard C. Landis, Ron Griffith, and Stephen H. Shoemaker (DuPont)	**DOE/METC/31185 —5390, DE97002156**

Development of an Integrated *in-situ* Remediation Technology

DOE Contract Number: DE-AR21-94MC31185

Draft Topical Report for *Task No. 9-Part II Entitled:*

"TCE Degradation Using Non-Biological Methods"

Robert G. Orth and David E. McKenzie
Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167

Submitted by:

Monsanto Company
St. Louis, Missouri 63167

Abstract: Contamination in low permeability soils poses a significant technical challenge to in-situ remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing in-situ treatments such as bioremediation, vapor extraction, pump and treat rather ineffective when applied to low permeability soils present at many contaminated sites. The technology is an integrated in-situ treatment in which established geotechnical methods are used to install degradation zones directly in the contaminated soil and electro-osmosis is utilized to move the contaminants back and forth through those zones until the treatment is completed. The use of zero valence iron for reductive dechlorination of aliphatic chlorinated hydrocarbons is currently under investigation by a number of research groups as a potential method of in-situ treatment of contaminated ground water. The reaction appears to involve the transfer of electrons to chloro-aliphatic compound by the oxidation of zero valent iron to ferrous iron (Fe^{+2}). Our studies have indicated that this reaction is consitent with those of corrosion, and as such, can be influenced or increased by the presence of small amounts of the metals (0.5% by weight) such as copper, silver, gold and palladium coated on the iron surface. Incomplete coverage of the iron surface with a more electropositive metal results in an open galvonic cell, which increases the oxidation of iron and facilitates and increases the concurrent reduction of trichloroethylene and other chlorinated aliphatic compounds to the corresponding alkenes and alkanes. Our results show that plating more electropositive metals onto certain iron surfaces results in approximately a factor of ten increase in the dechlorination rate of small organochlorine compounds such as TCE.

A563	Ambersorb 563 sorbent (Rohm and Haas)
Ag	Silver
Au	Gold
BET	Brunauer - Emmett-Teller
Cl	Chlorine
CCl_4	carbon tetrachloride
CH_2Cl_2	methylene chloride, dichloromethane
Co	Cobalt
Cu	Copper
$CuSo_4.5H_2O$	Copper sulfate penta hydrate
CVOC	chlorinated volatile organic compound
CZE	Capillary Zone Electrophoresis
DCM	methylene chloride, dichloromethane
DOE	Department of Energy
ECD	electron capture detector
EPA	Environmental Protection Agency
EPCM	engineering, procurement and construction management
Fe	Iron
FID	flame ionization detector
GC	gas chromatography
GE	General Electric Company
H	Henry's law constant
HCl	hydrochloric acid
MC, $MeCl_2$	methylene chloride, dichloromethane
MeOH	methanol
Mg	Magnesium
Ni	Nickel
N_2	nitrogen
NA	not available
NDL	No detectable loss

PCE	perchloroethylene, tetrachloroethylene
PVC	polyvinyl chloride
$SnCl_2$	Stanoues chloride
Sn	Tin
S	Sulfur
TCE	trichloroethylene
VOC	volatile organic compound
Zn	Zinc

C, °C	Celsius, degrees Celsius
cc	cubic centimeters
cm	centimeters
d, D	days
deg	degrees
g	grams
h, hr	hours
k, K	thousand
kcal	kilocalorie
kg	kilograms
l, L	liters
M	molar (moles/liter)
m	meter
mg	milligrams
min	minutes
ml, mL	milliliters
mM	millimolar (millimoles/liter)
mm	millimeters
mmol, mmole(s)	millimole(s)
mol	mole(s)
mw, MW	molecular weight
N	normal (equivalents/liter)
ppb	parts per billion
ppm, ppmw	parts per million (by weight)
ppmm	parts per million (molar)
ppmv	parts per million (by volume)
RPM	revolutions per minute
μg	micrograms
μl, μL	microliters
μm	micrometers
μM	micromolar (micromoles/liter)

μmol, μmole(s)   micromole(s)

yr   year

D. Table of Contents

Statement of the Problem

Contamination in low permeability soils poses a significant technical challenge to *in-situ* remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing *in-situ* treatments such as bioremediation, vapor extraction, and pump and treat, rather ineffective when applied to low permeability soils present at many contaminated sites.

The Solution

The proposed technology combines electro-osmosis with treatment zones that are installed directly in the contaminated soils to form an integrated *in-situ* remedial process. Electro-osmosis is an old civil engineering technique and is well known for its effectiveness in moving water uniformly through low-permeability soils with very low power consumption.

Conceptually, the integrated technology could treat organic and inorganic contamination, as well as mixed wastes. Once developed, the technology will have tremendous benefits over existing ones in many aspects including environmental impacts, cost effectiveness, waste generation, treatment flexibility, and breadth of applications.

Consortium Description

A Consortium has been formed consisting of Monsanto, E. I. du Pont de Nemours & Co., Inc. (DuPont) and General Electric (GE), with participation from the Environmental Protection Agency (EPA) Office of Research and Development and the Department of Energy (DOE). The five members of this group are leaders in their represented technologies and hold significant patents and intellectual property which, in concert, may form an integrated solution for soil treatment. The Consortium's activities are being facilitated by Clean Sites,

Inc., under a Cooperative Agreement with EPA's Technology Innovation Office. A schematic diagram of the government/industry consortium is shown on the front page of this topical report.

Management Plan

A Management Plan for this project was prepared by Monsanto and submitted on November 30, 1994. That plan summarized the work plan which was developed in conjunction with DuPont, GE, EPA's Risk Reduction Engineering Laboratory (RREL), Martin Marietta Energy Systems (MMES), and the Department of Energy. The DOE Gaseous Diffusion Plant in Paducah, Kentucky, has been chosen as the site for the initial field tests.

CDM Federal Programs Corporation was chosen to provide the on-site support of the field tests which were installed at the DOE site in November 1994. This experiment tested the combination of electro-osmosis and *in-situ* sorption in the treatment zones. In 1994 and 1995, technology development was carried out under the present contract by Monsanto, DuPont, and GE. These studies evaluated various degradation processes and their integration into the overall treatment scheme at bench and pilot scales.

Technical Deliverables

Tables 1 and 2 summarize the 13 technical tasks and the 8 topical reports which will be written describing the results obtained in the technical tasks. These two tables show which organization is primarily responsible for the tasks and for preparing the topical reports. ***The present topical report summarizes Task No. 9-Part II - TCE Degradation Using Non-Biological Methods.***

Table 1. List of Tasks and Responsible Company

Task	Company
Task 1 - Evaluation of Treatment Zone Formation Options (5.1.2)	DuPont
Task 2 - Electrokinetic Model Validation and Improvement (6.5)	GE
Task 3 - Design Guidance for Field Experiments (6.6)	GE/DuPont
Task 4 - Analysis of Electrode Geometry and Soil Heterogeneity (6.7)	GE/DuPont
Task 5 - Cost Analysis (7)	Monsanto/DuPont
Task 6 - Lab-Scale Development of Microbial Degradation Process (8.1.2)	DuPont
Task 7 - Lab-Scale Electrokinetic and Microbial Degradation (8.1.6)	Monsanto
Task 8 - Lab-Scale Tests of Lasagna Process Using DOE Paducah Soil (8.1.7)	Monsanto
Task 9 - TCE Degradation Using Non-Biological Methods (8.2.1, 8.2.2.2, 8.2.3.2)	GE/Monsanto
Task 10 - Bench- and Pilot-Scale Tests (9.3)	Monsanto
Task 11 - Establish Contamination Conditions Before and After Tests (10.1.2)	DuPont/MMES
Task 12 - Design and Fabrication of Large-Scale Lasagna Process (12.1, 12.2)	Monsanto/DuPont/Nilex
Task 13 - Large-Scale Field Test of Lasagna Process (12.3, 12.4)	Monsanto/CDM

Table 2. List of Topical Reports and Responsible Company

Topical Report	Company
Task 1 - Evaluation of Treatment Zone Formation Options	DuPont
Tasks 2 - 4 Electrokinetic Modeling	GE
Task 5 - Cost Analysis	Monsanto
Task 6 - Laboratory-Scale Microbial Degradation	DuPont
Tasks 7, 8, 10 - Bench- and Pilot-Scale Tests of Lasagna Process	Monsanto
Tasks 9 - TCE Degradation Using Non-Biological Methods	GE
Task 11 - Contamination Analysis, Before and After Treatment	Monsanto
Tasks 12 and 13 - Large-Scale Field Test of Lasagna Process	Monsanto

INTRODUCTION

The use of zero valent iron to dechlorinate chlorinated hydrocarbons has been of increasing interest for use in in-situ remediation over the past 5 years. The prospect of using zero valent iron in the treatment zones in Lasagna initiated studies in our laboratory for the determination of the mechanism of the dechlorination and for the search as to how the rate of the process may be improved. The studies included the examination of the electrochemical nature of the dechlorination process and utilized high purity iron and iron combined with different metal. The rates of the reaction were monitored and the products produced were determined so as to obtain a mass balance. The effect of iron combined with clay soils was also examined using batch methods but mass balances were not carried out in these cases. In addition, experiments examined a wide range of halogenated hydrocarbons as represented by priority pollutants. Extensive studies of column systems were carried out by GE and are reported by them separately.

The results will be divided into three separate experiments: 1) iron and iron plus other metal mixtures; 2) iron and metal mixtures with priority pollutants: and 3) plating of iron with metals that have higher reduction potentials and the dependance of rate on coverage.

There are many studies that indicate that iron dechlorinates chlorinated hydrocarbons such as TCE (1-5). Studies using metals to dechlorinate hydrocarbons in the gas phase were reported by Crummit et el. (6). There are also patents (7,8) that suggest the use of iron for dechlorination in waste streams. The mechanism has been clearly shown to be a surface controlled process and that it is an electrochemical process. There is some discussion as to if the fundamental processes involve one electron process or two electron process. Our results will indicate that the process is a corrosion process and that rates can be controlled by the same techniques observed in corrosion chemistry.

A consortium of industry (Monsanto, Dupont and General Electric) was formed in collaboration with the Department of Energy (DOE) and Environmental Protection Agency (EPA) to combine expertise and resources for accelerating the development of this technology. The collaboration led to a field experiment of the Lasagna process at a DOE site in Paducah, KY, that has clay soil contaminated with trichloroethylene (TCE). The Paducah Gaseous Diffusion Plant (PGDP) site was chosen from a list of Department of Energy sites based on two major criteria: low-permeability soil and a single chlorinated contaminant without heavy metals or radionuclides. DOE contributed by providing the contaminated site in Paducah for the test, soil sampling and analysis support (through Martin Marietta), and funds through a Research and Opportunity Announcement (ROA) grant. The entire project, including laboratory research and field work was about one million dollars. Since the Lasagna process includes treament zones which can utilize absorbants as in the case for the Field study or reactive zone, then it is necessary to understand the results of any reactive systems that maybe used in the treatment zones. This report documents the contribution of Monsanto to the studies of the degradation of TCE using non-biological methods and concentrates mainly on the use of zero valence iron and what process may be used to increase the rate of dechlorination.

Objectives of the Studies for TCE Degradation Using Non-Biological Methods

The purpose of these studies was to determine what factors control the processeses of TCE dechlorination when using zero valent iron and to determine if certain irons could be modified to increase the reactions rates. Since it is possible that in the second phase of the Paducah field study, that reactive treatment zones would be used instead of absorbent treatment zones, it is necessary to understand the mechanism of the dechlorination process and what effects the rates of the process. In addition, it is necessary to know what the products of the dechlorination process are so that problems are not created from the treatment zone.

Mixed Metal Studies

Materials List Mixed Metal Experiments.

High purity iron 99.999% obtained from Aesar

Mallinckrodt iron 100 mesh

Stannous Chloride purchased from Mallinckrodt

Copper Metal electrolytic dust obtained from Fisher scientific

Nickel reduced powder obtained from Fisher Scientific

Magnesium metal (40-80 mesh) obtained from Fisher Scientific

Tin powder certified obtained from Fisher Scientific

Zinc granular 30 mesh obtained from Fisher Scientific

Cobalt powder obtained from Fisher Scientific

Trichloroethylene (99+%) obtained from Aldrich chemical company

12 mL National Scientific company vials with Teflon/silicone septum obtained form

    Fisher Scientific

Tube Rotator obtained from Scientific Equipment Products

Experimental

A batch experimental approach was used in the mixed metal studies. Initially, Aesar pure iron (1g) was weighed into eight 12 mL vials equipped with Teflon faced septa. The other metal (tin, copper, zinc etc.) was then weighed into the appropriate vial. These weights were held constant at 0.05 g per other metal. A water solution was then prepared by combining 250 mL water and 50 uL 88% formic acid. 10 mL of this water was then pipetted into each vial. Each vial was then spiked, subsurface with 0.5 uL Trichloroethylene (TCE) with a 5 uL Hamilton syringe. Immediately after spiking the vials were capped. Vials were then placed on a tube rotator at 18 RPM. A reagent blank also containing 1 g Aesar iron and no TCE and a simulated spike containing the reagent water and TCE was also placed on the rotator. The experiment was started on 11/3/93 at 9:40 AM. The vials were sampled periodically until 11/9/93 at 4:00 PM by removing 100 uL of the solution with a repeater pipette and placing it directly into 10 mL of hexane. After sampling the group of experiments the vials were placed back onto the sample rotator, until the next sampling period.

In each batch experiment a set of experiments were run so that relative comparisons could be made within a set. The sets consisted of the Fe metal for which the comparison was to be made at a certain mass and a control vial containing TCE but no metals. Since TCE has a relatively large partial pressure in water, all rates were determined relative to the vial containing TCE and no metal. This vial is referred to as the simulated spiked sample. Each point was then plotted relative to the loss of TCE in the control. In other words the measured concentration of a reaction was divided by the measured concentration in the simulated spike to correct for volatility losses for each sampling time. C_o can be defined as the initial concentration determined for a reaction mixture corrected for volatility losses at each sampling time. C_i/C_o is the normalized concentration of the reaction versus the simulated spiked sample, where C_i is the measured concentration of the reaction mixture. The simulated spiked sample was sampled each time the reaction mixtures were sampled and this correction was made for each reaction mixture data point. The control was assumed to have the same loss during sampling as the samples. The mass of the metal was always maintained the same within a set of experiments, since the rates depend on surface area and therefore the mass used then comparisons of rate increases are made against a control of Fe having the same mass.

Analytical procedures

The analysis for TCE was typically carried out on a gas chromatograph equipped with an electron capture detector (GC/EC). This is a highly sensitive technique for determination of chlorinated compounds. The gas chromatograph was an HP 5890 equipped with a 30 meter x 0.53 um Supelco 2 5320 column. The temperature program was; initial temperature was 40°C held for 4 minutes followed by an increase to 65°C at a rate of 10 degrees per minute followed by an increase to 200°C at a rate of 30 degrees per minute. The output of the GC/EC was controlled by a Dionex data system. Quantitation was carried out against a standard curve.

Results

The ln C_i/C_o was plotted vs time. A plot of this nature indicated if the rate is a pseudo first order reaction. The plots indicated that the reactions were all pseudo first order and therefore comparisons based on pseudo first order half lives could be made. This was accomplished by fitting the data with a linear least squares fit and obtaining the rate constant k for the mixed metal. The half-lives were calculated from $t_{1/2} = \ln2/k$.

Table 2 shows the half-lives calculated by this approach. The results in the Table 2 indicate that the addition of copper decreases the time to lose half of the TCE to 10 hours from 69 hours observed for pure Fe. Table 2 also indicates that the decrease in half-life with the addition of Cu metal is independent of the amount of metal added. That is 0.5 % by weight of Cu yields within experimental error the same half-life as a mixture of Fe and Cu containing 50 % Cu. The other observation from Table 2 is that the presence of Ni metal also decreases the half-life of the loss of TCE. The Ni shows a delay in a loss in TCE which can be seen in the plot of the data in Figure 1. The half-life that is calculated is based on the changing portion of the curve. The line in Figure 1 is the pseudo first order fit to the data. The observation that Cu and Ni increases the rate suggest that any metal that has a more positive reduction potential than iron will increase the rate of loss of halogenated hydrocarbons such as TCE. This observation holds only if the metals with more positive potentials can plate on the iron or through a mechanical mechanism to placed in contact with the iron. The process of plating can occur through the dissolution of the metal which immediately plates on the surface of the iron because of the positive reduction potential with respect to iron. This can be seen with the Cu and Ni which have higher reduction potentials than the Fe.   The contact causes a cathodic and anodic potential to occur at the surface

increasing the rate of loss of TCE. The rate increase for Cu was 7 times that observed for pure iron. For the Ni the rate increase was 1.5 times with respect to the iron. If the contact with the surface cannot occur then the increase of the rate of loss of TCE will not occur. Sn and Co have more positive reduction potentials but did not give an increase in rate of loss with respect to Fe. These metals can be placed directly on the surface by using salts by electrode less processes. Once placed directly on the surface there should be an observed rate increase.

To show that the plating directly would improve the rate of loss of TCE, 0.1g of $SnCl_2 . 2 H_2O$ was dissolved in .01N HCl solution. 30 grams of Mallinckrodt iron 40 mesh was placed in 100 mL of water and stirred rapidly under a blanket of nitrogen. The Sn^{+2} solution was added rapidly to the stirred reactor. This process plated Sn onto the surface of the iron. The amount of tin was calculated to give a surface coverage much less than a monolayer based of a surface area of the iron of 0.5 m^2/g as determined by BET measurements. The nitrogen was necessary since the exposed iron surface will corrode at an accelerated rate with a partial coverage of Sn. Water was removed from the reactor and the tin plated iron washed several times with water followed by acetone. The tin plated iron was dried under a stream of nitrogen. The experiment was run against Mallinckrodt iron 40 mesh iron having no Sn plated with a TCE control which contained no metal. The control contain 200 ppm of TCE and this was placed in a 12 mL vial and capped with a Teflon line top. 7 grams of the tin plated iron was placed in a 12 mL vial and the vial filled with 200 ppm TCE solution so that no headspace existed. To a third 12 mL vial 14 grams of the tin plated iron was added and filled to the top with 200 ppm solution of TCE. To a fourth 12 mL vial 7 grams of the iron was added and the vial fill with 200 ppm solution of TCE. The iron was prepared the same as the tin:iron except that no tin was added to the stirred reactor.

Table 2 shows the results of the plating of tin onto iron. The tin plate increases the rate by a factor of 7. Table 2 also shows that the rate depended on the amount of tin on plated iron indicating a surface dependence. This also indicates that in the metal mixture in Table 1 no plating or surface contact was occurring in the Fe:Sn mixture.

Table 1. Half-lives for mixed metal experiments.

	99.999% Fe	Fe:Cu (0.5%) run in duplicate	Fe:Cu (25% Cu)	Fe:Cu (50%Cu)	Fe:Ni	Fe:Co	Fe:Sn	Fe:Zn	Fe:Mg
first order half-life (hr)	69	9.8	10	9.5	44	NDL*	NDL*	NDL*	NDL*

* NDL = no detectable loss of TCE during experiment

Table 2. Rate increase due to Sn plate on iron.

	Fe (7 grams)	Fe plated Sn (7 grams)	Fe plated Sn (14 grams)	TCE control
concentration TCE ppm at 24 hours	143	19	0.04	190 ppm
half-life (hr)	49	7	2	

Figure 1. Fe:Ni mixture
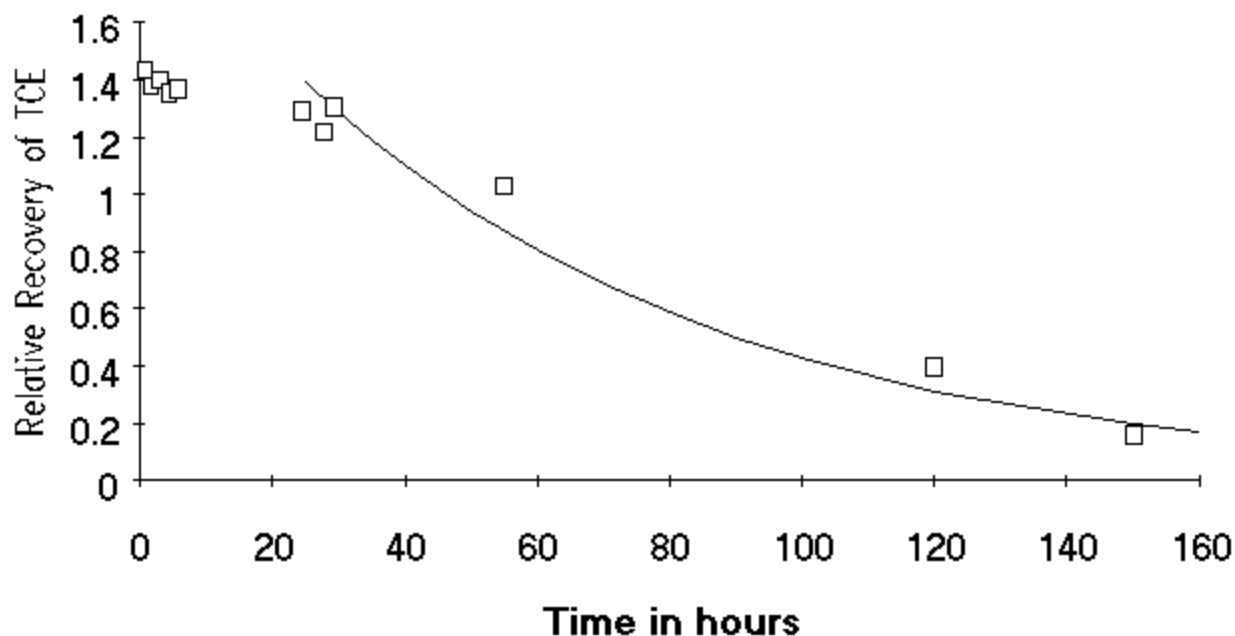
Zero Valance Iron and iron metal mixture Dechlorination of Priority Pollutants

Materials list / Priority Pollutant Standard

Volatile Priority Pollutant Standards obtained from Restek Corporation (Catalogue numbers 30007, 30008, 30009, and 30010) with each component at 2000ug/mL. Individual halogenated compounds are listed in the table containing Comparison of half-lives between different mixtures of inorganics with iron.

Iron powder (100 mesh) from Mallinckrodt 99.2% purity

Formic Acid (88%) obtained from Fisher Scientific.

Teflon Caps obtained from Fisher Scientific

4 oz bottle obtained from Fisher Scientific

Cupric sulfate pentahydrate obtained from Fisher Scientific

Ferrous sulfate heptahydrate obtained from Fisher Scientific

Sulfur obtained from Fisher Scientific

Copper metal obtained from Fisher Scientific

Experimental

Restek calibration standards Mix 2 through 5 were combined resulting in a 500 ppm mixture of the volatile priority pollutants. One liter of Milli-Q water was spiked with 48 uL 88% formic acid to be used as reagent water. Mallinckrodt Iron (6 g) was weighed into six 4 oz (120 mL) sample bottles. One

bottle was chosen as a control containing no iron and only water and the volatile priority pollutants. Copper metal (1 g) was weighed into one bottle containing iron, and cupric sulfate pentahydrate (1.26 g and 0.44 g) was weighed into two other bottles containing iron. Sulfur (0.1 g) was weighed into one bottle containing iron and 0.4 g ferrous sulfate was weighed into another bottle.   Another bottle containing no iron was selected to serve as a simulated spiked sample. To each bottle 100 mL of reagent water were added. The bottles were capped and shaken. Each reaction mixture was uncapped and spiked subsurface with 400 uL of the volatile priority pollutant standard mixture and capped. The bottles were placed on a Lab Line Orbit Environ Shaker and rotated at 150 RPM. Vials were removed for sampling and 2 mL were removed and added to a 1.5 mL autosampler vial equipped with Teflon Faced septum. The auto sampler vials were filled until they overflowed and were then capped to minimize headspace. This was done to minimize loss of the highly volatile components. Reaction mixtures were sampled at 23.13 hours, 46.78 hours, 54.38 hours, and 71.66 hours respectively.

In each batch experiment a set of experiments was run so that relative comparisons could be made within a set. The sets consisted of the Fe metal for which the comparison was to be made at a certain mass and a control vial containing the volatile organic priority pollutants but no metals. Because many of these compounds have a relatively large partial pressure in water it was necessary that all rates be determined relative to the vial containing water, the compounds and no metal. This vial is referred to as the simulated spiked sample. The mass of the metal was always maintained the same within a set of experiments, since the rates depend on surface area and therefore the mass. The same procedure for determining the rate of the reaction was carried out in these experiments as in the experimental procedure for the metal mixtures. That is plots of ln C_i/C_o versus the sampling times indicates pseudo first order rates. Linear least squares fit of the data provide the rate constant and from the rate constants' half-lives can be calculated using $t_{1/2}=Ln(2)/k$. In some cases the reactions were so rapid that only one data point could be obtained. In these cases the reaction was assumed to be pseudo first order and a rate constant and half life calculated from that point. In some cases the reaction was so rapid that at the first sampling time of 23.13 hours there was no detectable signal. Again the reaction was assumed to be pseudo first order and a maximum rate constant and half-life calculated based on the detection limit for that compound. For both of these cases the half-lives are indicated with a less than symbol.

Analytical procedures

Analyses were performed using a Tekmar Liquid Sample Concentrator LCS-2 interfaced with a Hewlett Packard 5890 gas chromatograph with a Hewlett Packard 5970 mass selective detector. This technique is referred to as purge and trap analyses. Generally, the technique involved adding 0.3 mL of the samples from the 1.5 mL autosampler vials to 10 mL purge and trap tubes which had 5 mL deionized water in them , which were then sequentially sparged with 30 mL/ minute helium onto a Supelco-1-2547 1% SP-1000 60/80 mesh carbopack B 8" X 1/8" stainless steel trap column at 27°C. The trap column was desorbed for 8 minutes at 200°C onto the chromatographic column which was held at 10°C during the desorb cycle.

Separation was performed using a 30 m J&W DB-624 0.53 mm I.D. with 0.25 uM film thickness column. The chromatographic conditions employed were a starting temperature of 10°C which was held for 6 minutes followed by ramping the oven at 10 degrees per minute until 200°C. The oven was held at the final temperature for 5 minutes.

Mass spectral data were collected from 30 to 350 amu for the duration of each run. Concentrations were determined by comparing the results to a standard curve using a Hewlett Packard UNIX based data system equipped with Throughput Target data reduction software.

Results

Table 3 shows the half-lives obtained for each compound in the chemical mixture for the different Fe combinations. The first point to notice is that the benzene and chlorobenzene did not show any loss for any combination indicating that these are not affected by the Fe or the Fe combinations under the conditions studied. The Fe:Cu metal mixture showed a detectable increase in the rate of dehalogenation as indicated by a lower half-life for most of the compounds when compared to iron. For some of the chlorinated compounds no loss was detected, but the experiment were not run long enough to detect loss of these compounds with Fe. For example, 1,2-dichloroethane showed no detectable loss for the Fe and Cu metal mixture.

The addition of $CuSO_4 \cdot 5H_2O$ to the water containing Fe causes the Cu to plate onto the Fe surface. The more $CuSO_4 \cdot 5H_2O$ added to the solution the more Cu that plates onto the Fe surface. Therefore there is more Cu plated onto the Fe surface for 1.2g $CuSO_4 \cdot 5H_2O$ as compared to the 0.44 g $CuSO_4 \cdot 5H_2O$. In comparing the $CuSO_4 \cdot 5H_2O$ experiments with the Fe and the Fe:Cu in Table 3, it can be seen that for the Fe:Cu metal mixture all halogenated hydrocarbons showed significant improvement for the rate of dehalogenation. For many the improvement was that the rates went from no detectable loss over the time period of the experiment to half-lives that were less than 4 hours. This was the case for cis-1,2-dichloroethene. Where measured comparisons could be made between the Fe and the Fe $CuSO_4 \cdot 5H_2O$ (1.2g) the improvement was >20 times the rate observed for Fe. Also noted in Table 3 is that where detectable half-lives were measured, the comparison between the lower $CuSO_4 \cdot 5H_2O$ (0.44) and the $CuSO_4 \cdot 5H_2O$ (1.2g) showed a longer half life for the lower coverage. There was one exception to this observation with 1,2-dichloroethane where the half-life increased for the higher coverage Fe($CuSO_4 \cdot 5H_2O$(1.2g)). Chloromethane showed no improvement when comparing the metal mixture of Fe:Cu and the Fe:($CuSO_4 \cdot 5H_2O$) mixtures. Comparisons were difficult because of the high uncertainty in the half-life. This uncertainity was caused by the high volality of this compound.

Decreases in half-lives when compared to the Fe can be seen with the Fe:$FeSO_4$ mixture. These rates were significantly less than the improvements noted for the Fe:($CuSO_4 \cdot 5H_2O$) mixtures. For many cases no decrease could be measured. The Fe:S mixture did show decreases in the half-lives for many but not all of the compounds.

The point that can be made with regard to this experiment is that significant increases in rates can be obtained by plating Cu onto Fe. The rate increases can be as high as 20 times. The amount of Cu on the Fe surface affects the rate and an improvement was noted as the amount of Cu was increased. These experiments also support the point that it is necessary to have anodic and cathodic potentials on the surface of the Fe. This increases the rate of the dehalogenation.

Table 3. Comparison of half-lives (hours) between different mixtures of inorganics with Iron

	Fe	Iron with Cu metal	Fe with CuSO$_4$, 5H$_2$0 (1.2g)	Fe with CuSO$_4$, 5H$_2$0 (0.44g)	Fe with FeSO$_4$	Fe with S
1,1,1-trichloroethane	22	10	<4*	<4*	17	11
1,1,2,2-tetrachloroethane	112	8	<4*	<4*	59	33
1,1,2-trichloroethane	NDL	12	<4*	<6*	NDL	NDL
1,1-dichloroethane	NDL	37	17	NDL	NDL	NDL
1,2-dichloroethane	NDL	NDL	121	32	NDL	NDL
1,1-dichlroroethene	49	18	<3*	8	22	26
cis-1,2-dichloroethene	NDL	NDL	4	8	NDL	NDL
trans-1,2-dichloroethene	NDL	42	<1*	4	167	49
trichloroethene	NDL	102	7	32	NDL	26
tetrachloroethene	NDL	52	10	35	NDL	44
vinyl chloride	NDL	64	5	6	NDL	NDL
bromodichloromethane	5	8	<4*	<4*	<11*	<4*
bromoform	<6*	<5*	<4*	<4*	<7*	<6*
bromomethane	62	21	20	19	158	28
carbon tetrachloride	23	10	<5*	<5*	24	10
chloromethane	NDL	164	146	93	196	NDL
cis--1,3-dichloropropene	8	9	<3*	<3*	<11*	<4*
trans-1,3-dichloropropene	14	<10*	<3*	<3*	<15*	<3*
methylene chloride	NDL	NDL	69	NDL	NDL	NDL
benzene	NDL	NDL	NDL	NDL	NDL	NDL
chlorobenzene	NDL	NDL	NDL	NDL	NDL	NDL

* Maximum half lives based on assumption of psuedo first order   NDL = No detectable Loss

Materials List Coverage Study and the use of other more positive reduction metals

Iron powder (100 mesh) from Mallinckrodt 99.2% purity

Teflon Caps obtained from Fisher Scientific

8 mL bottle obtained from Fisher Scientific

Cupric sulfate pentahydrate obtained from Fisher Scientific

Tube Rotator obtained from Scientific Equipment Products

Cupric nitrate dihydrate obtained from Fisher Scientific

B&J Hexane

Trichloroethylene (99+%) obtained from Aldrich chemical company

8 mL National Scientific company vials with Teflon/silicone septum obtained form Fisher Scientific

Ag_2SO_4 purchased from Aldrich

$AuCl_3$ purchased from Aesar

Experimental

The study with the mixtures of halogenated compounds indicated that the amount of Cu on the iron surface affects the rates of the reaction. As the amount increased the rate increased. In those experiments no effort was made to coat the Fe surface uniformly. Thus how the coverage affected the rates could not be easily determined. To further test this observation an experiment to control the coverage was designed.

The plating of Cu metal on Fe was carried out in a way to try to obtain a uniform plating of the iron. To do this any technique used must maintain a highly stirred system. To plate the iron, $CuSO_4 \cdot 5H_2O$ was dissolved in water. The Cu^{+2} was agitated rapidly as 30 grams of Mallinckrodt Iron were added to the solution. The amount of Cu^{+2} to be plated was varied so that the coverage of the iron would be less than a monolayer to well over a monolayer. In determining the concentration of Cu^{+2} to use, it was assumed that the Cu atom on the surface was a sphere with an atomic radii of 1.1 angstroms. The surface area of the iron as determined by BET measurements using Ar gas was 0.5 m^2/g for a total of 15 m^2 for the 30 grams of Fe. Thus 0.1 grams of $CuSO_4 \cdot 5H_2O$ would yield 0.59 of a total monolayer coverage of the surface. Considering that Cu can plate on itself this coverage is an over estimate of the coverage and the actual coverage was <0.59 of a monolayer coverage of the surface. A 1.1 gram sample will increase the coverage to < 7 monolayers. The 5 grams $CuSO_4 \cdot 5H_2O$ should give a coverage of < 50 monolayers. The coverage can also be confirmed by visual inspection of the iron. With less than a monolayer the Cu is not visible. As the coverage increases the Cu red color begins to appear. At the highest coverage the metal appears to be copper with some iron present. At a coverage below a monolayer rapid corrosion of the iron begins if oxygen is present. To slow this process the plating was carried out under a nitrogen blanket.

TCE standards of 730 ppm solution were made by adding 125 uL TCE to 250 mL water. Cu coated Fe (5 g) was weighed into an 8 mL vial. This was repeated for each of the three different Cu plating concentrations. Another bottle containing no iron was selected to serve as a simulated spiked sample. A vial containing the 5 grams of iron treated in the same manner as the Cu coated but containing

no Cu was prepared so that comparison of the rates could be made. To each vial TCE solution was added to the top and capped. The bottles were placed on a Tube Rotator and rotated at 18 RPM. Vials were removed for sampling and 0.1 mL removed and extracted into hexane following the procedure outlined in the section describing the metal mixture experiments.

Data were examined in the same manner described in the previous studies.   That is, plots of ln C_i/C_o versus the sampling times indicates pseudo first order rates. Linear least squares fit of the data provide the rate constants and from the rate constants half-lives were calculated using $t_{1/2}=Ln(2)/k$.

Analytical procedures

Determination of the concentration of TCE was carried out using the methods described in the analytical section of the metal mixtures. Chloride determinations were made using Capillary Zone Electrophoresis methods provided by Dionex. The CZE instrument was a CZE Dionex CES 1.

Results

Table 4 shows the pseudo first order half-lives for each of the experiments. As can be seen from Table 4 the rate increases for a coverage less than half of the surface. As the coverage increases the rate begins to slow until at the highest coverage examined the rate has decrease to 40% of the highest rate observed in this series.   Higher increases in rates with respect to iron were observed for the studies involving the mixture of halogenated compounds. But the coverage was not carefully controlled and the amount of available iron surface was probably larger. This would indicate that the 0.59 monolayer coverage would not be the maximum rate. Thus the rate for lower coverage would be faster and the 0.59 monolayer would not be the maximum rate. Studies with pure Cu metal with no Fe present showed no loss of TCE over time periods of 100 hours. This would clearly indicate that once the iron is completely covered by many monolayers of Cu the dehalognation reaction would not occur.

Another copper salt tried was $Cu(NO_3)_2 \cdot 2H_2O$. Table 5 indicates that the use of this salt still provided the Cu^{2+} ions in solution for plating on Fe. The use of the nitrate salt can make it more difficult to control the uniformity of the Cu plating because of the nitrate oxidation potentials. This can be seen in Table 5 by the increase in rates as the amount of $Cu(NO_3)_2 \cdot 2H_2O$ used with 30 grams of Fe increased. At similar levels using the $CuSO_4 \cdot 5H_2O$ the iron took on the appearance of Cu.   With the $Cu(NO_3)_2 \cdot 2H_2O$ the Cu could not be seen on the surface of the Fe. This means that the amount of Cu salt used to give the optimum coverage can vary with the salt used. Table 5 also shows the chloride produced during the reaction time indicating that within experimental error 3 moles of Cl^- were produced for each mole of TCE lost indicating a stoichiometric dechlorination. Headspace studies indicated that the carbon products were ethene, ethane, propene, propane, and small amounts of C_4 to C_6 hydrocarbons. The carbon balance was found to be greater than 90% based on these measured hydrocarbons.

Salts of Ag and Au were also examined. These metals have a higher reduction potential than Fe and should plate onto iron. The amount of Ag and Au salt used was calculated to be sure that the coverage of the surface would not exceed 1 monolayer for 30 grams of Fe. For this study the Fe:Cu with a coverage calculated to be <0.6 monolayer Table 4 was utilized. As in all studies an Fe control was run along with a simulated spike. These experiments were run in the same manner as the previous experiments except that 10 grams of metal were added to the 8 mL vials. The half-lives were determined from the pseudo first order rate constants are shown in Table 6. As was observed previously if the amount of metal is increased the rate increases. The rate for the Fe:Cu <0.6 monolayer was faster than that observed when 5 grams were used (see Table 4). The same occurred for the Fe. Ten grams of iron had a half-life of 53 hours compared with the 111 hours shown for 5 grams in Table 4. The rates for the Ag and Au both show a marked increase over the Fe. The improvement is comparable to that observed for the Fe:Cu.

Table 4. Variation in half-life as coverage increases

Calculated Monolayer on Fe surface	Observed half-life (hours)
0	111
0.59	30
<7	37
<30	48

Table 5. Observed half-life for Cu plated on Fe using Cu(NO$_3$)$_2$ 2H$_2$O and Chlorine mass balance.

Sample ID (amount grams Cu(NO$_3$)$_2$, 2H$_2$O added to 30g Fe)	half-life hours	Amount TCE lost umole/mL	Amount Cl$^-$ produced umole/mL	mole ratio Cl$^-$/TCE
Fe	149	1.77	5.5	3.1
Fe:Cu (0.1g)	63	3.1	6.6	2.1
Fe:Cu (1 g)	51	3.6	12.6	3.5
Fe:Cu (5g)	12	5.28	14.7	2.8

Table 6. Half-life metals plated on iron.

Sample ID	Half-life (Hours)
Fe	53
Fe:Cu (<0.59 monolayer)	17
Fe:Ag	10
Fe:Au	17

ACKNOWLEDGMENTS

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